SYNTHESIS AND CHARACTERIZATION OF CERAMIC NANOFLUIDS

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By

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and characterization of ceramic Nanofluids** "submitted **by Anubhav Patra (111MM0398)** and **Aditya Narayan S.S Swain (111MM0407)** in partial fulfilment of the requirements for the award of BACHELOR OF TECHNOLOGY Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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ABSTRACT

With the advent of the century of “nano”, it is evident that we are heading towards miniaturization of technological equipment and electronic circuits. This has ultimately resulted in problem in heat dispersion from the system. This situation demands for better cooling facilities and using of nano-fluids as coolant is undoubtedly the optimum solution. This project dealt with the usage of Silica nano-fluids as coolant and its various parameters. In pursuit of studying various aspects of using the silica nano-fluid as a coolant, in the present study a comprehensive experimental data set was obtained for thermal conductivity of nano-fluids with variation in Silica nano-particle volume fraction and base liquid (Water and Ethyl Glycol). SEM and Zeta-sizer study was done to confirm the uniformity in nano-particle size distribution. SEM study was also done to determine the grain size. The effect of pH change on the thermal conductivity of the nano-fluids was also taken into consideration. Amidst all these addition, the most important factor is the stabilization of the nano-fluids as they are prone to agglomeration due to its high surface energy. Thus, stabilization of the nano-fluids was manipulated by the addition of surfactant (Oleic Acid). Their related thermal conductivity was also studied. This project also considered the stabilization process by visual observation over a period of 24 hours.

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CHAPTER I: INTRODUCTION

The appearance of nano-fluid as a new field of nanoscale heat transfer in liquids is associated straight to miniaturization tendencies and nanotechnology. The recent technology demands cooling capabilities with better performance. The addition of metallic and metallic -oxide nanoparticles to coolants which are used in thermal control systems can intensely increase the thermal conductivity of the solvent. Such nanoparticle-fluid materials are referred to as" nanofluids" Fluids are often used as heat carriers in heat transfer equipment. Instances of significant usages of heat transfer fluids are in automotive, aeronautical cooling systems and manufacturing process heating and cooling systems. In all of these solicitations, the thermal conductivity of heat transfer fluids plays a vital role in the growth of energy-efficient heat transfer apparatus. In a dispersion, movement of nanoparticles is random and in this manner they carry comparatively large volumes of enveloping liquid with them. This micro-scale interfacing may occur between areas with a temperature gradient,subsequently resulting in a lowering of local temperature gradient for a given heat flux compared with the pure liquid case. Thus, as a consequence of Brownian motion, the actual thermal conductivity, k_{eff}, increases the traditional analysis of heat conduction for solid-in-liquid suspensions is thatof Maxwell, based on effective-medium theory. It is also known that metals and metal oxides in solid state have greater thermal conductivity than conventional fluids. Nanofluids are projected to display enhanced properties as compared to conventional heat transfer fluids. As heat transfer is prominent at the surface of the particle, greater surface area is desirable. Nanomaterials have remarkably large surface areas as compared to macro particles and hence they have a great importance in the applicability in heat transfer. The surface to volume proportion is high and it means that a very small volume fraction of dispersed nanoparticle can have a very high surface area, and is believed to significantly improve the heat transfer characteristics and stability of dispersions. Settling downis one of the major problem of nanofluids. The nanofluids stability depends on many factors such as, additives, *pH*manipulation and aggregation. The current work emphases on manufacture of silica nanoparticles using top –down approach and characterization of Nanofluid in different base fluid – water and Ethyl Glycol, estimation of thermal conductivity and stability of the nanofluids. Addition of surfactants such as oleic acid influences stability gives understanding on the development of better Nanofluid coolants.

CHAPTER II: LITERATURE REVIEW

2.1 Requirement of a coolant

Cooling system is mandatory for majority of heavy industries as well as for miniature electronic circuits. Conventionally, for industrial cooling purpose, required for heavy machinery, different grade of aqueous or organic liquids are used. Typical usages are heat exchanger (close loop use) or heat treatment shop quenchants (open loop use). For electronic circuits still air cooling is prevalent techniques. But liquid cooling system for such use is under research[1]. Theoretically, a good coolant is required to have the following properties

- High heat transfer characteristics(high thermal conductivity)
- High stability over a range of temperatures
- Less viscosity
- High specific heat
- High latent heat of evaporation
- Safe at working temperature
- Cost effective
- Reproducible

Conventional coolants have become obsolete in the present demand of industries. With new technological advancements and miniaturisation conventional coolants have been unable to keep pace with the demand of faster heat sinking. Research in this field in the past few decades have involved use of microscopic dispersions in the fluid to improve the conductivity. But the settling down and erosion were the major drawbacks of macro dispersions. With the advent of nanotechnology researchers saw a possible improvement in the coolants. This paved in the way for next generation coolants-“nanofluids.Nanofluids are Nano-sized particles suspended in liquids [2].

Three properties that make nanofluids advanced coolants are:

(i) Better thermal conductivity

(ii) Better single-phase heat transfer

(iii) Better critical heat

(iv) Improved stability as compared to macro -suspensions

Nanofluids are formed by one step or two step methods with initial creation of nanoparticles. Creation of agglomeration free nanoparticles is the major requirement for creating a good dispersion.A large array of Nanoparticles are now available to researchers such as multiwall carbon nanotubes (MWCNT) which is a major focus of ongoing research. The metallic nanoparticles like Cu, Au etc. and non-metallic compounds like oxide ceramics (Al2O3, CuO), nitride ceramics (AlN, SiN), carbide ceramics (SiC, TiC), SiO_2 etc. are generally used with base fluids. Common base fluids are oil, ethanol, water and ethylene glycol [3,4].

Table 2.1: Thermal conductivities of several solids and liquids

Thermal conductivities of various solids and liquids

	Material	Thermal conductivity (W/m K)
Metallic solids	copper	401
	aluminum	237
Nonmetallic solids	silicon	148
	alumina (Al_2O_3)	40
Metallic liquids	sodium (644 K)	72.3
Nonmetallic liquids	water	0.613
	ethylene glycol (EG)	0.253
	engine oil (EO)	0.145

2.2 Parameters that affect thermal conductivity of nanofluid

One of the most important parameters affecting heat transfer is the thermal conductivity. The conductivity is the highest heat transfer rate of each mentioned heat transfer mechanism [5]

1. **Nature of nanoparticle.**

   Nanoparticles have different properties, they may be either ceramic or metallic, and can show vast variation in conductivity.in a given base fluid the net conductivity can be varied widely because of selection of nanoparticles.

2. **Effect of the Base fluid.**

Base fluid is the main solvent and remains as a major proportion of the nanofluid.they may be engine oil, DI water, Ethyl Glycol Etc.

3. **concentration of nanoparticles**

It is believed that increasing concentration of nanoparticles will increase the conductivity, this is because of effective surface area increment.But the volume fraction is critical as it affects the viscosity too.

4. **Shape of nanoparticles**

The shape is another important parameter, meshing is seen in case of Cylindrical nanoparticlessuch as MWCNT and SWCNT showing enhanced conductivity than spherical dispersed Nanofluid.

5. **Charge on the surface of nanoparticles**

A net surface charge on the surface of the Nano particle is required, to create inherent repulsion between two particles and create a stable solution.

6. **Effect of additives on nanofluids**

Additives check sedimentation, and a variety of them are used to create a stable Nanofluid.

7. **Effect of temperature on Nanofluid**

Temperature is an important parameter .the nanoparticles are more sensitive to temperature variation than the base fluid. The main reason being increase in random motion of the particles (Brownian motion) along with decrease in viscosity.

8. **Acidity (*pH*) effect**

pH affects the surface charge of the nanoparticles and in turn affects Nanofluid stability

2.3 Mechanism of nanofluid

The uncommon heat transfer characteristics of nanofluids cannot be explained only by particle concentration and individual conductivity.

To account for theabnormalsurge of the thermal conductivity,*Keblinski et al*. And *Eastman et al*. came up with possible mechanisms [6,7]

- Brownian motion
- Molecular-level layering of the liquid at interface

- The nature of heat transport in the nanoparticles

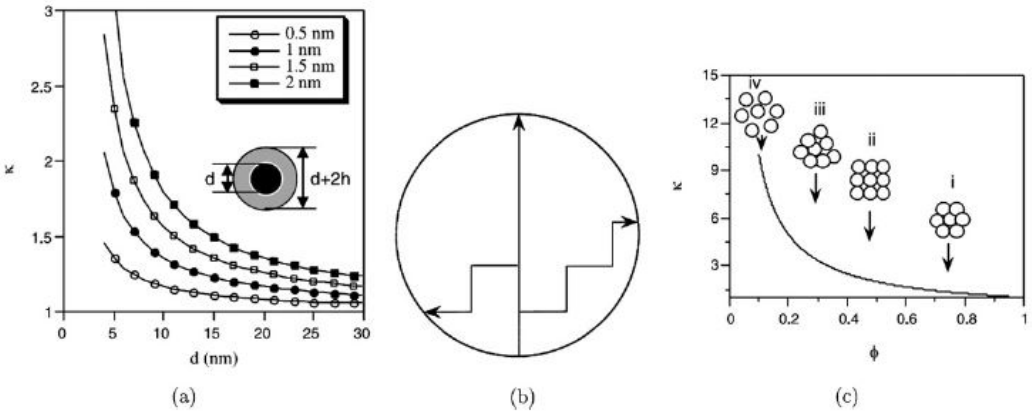

Fig. 2.1: Schematic diagrams a) Enhancement of *k* due to formation of highly conductive layer-liquid structure at liquid/particleinterface; (b) Ballistic transport in a solid particle; (c) Enhancement of *k* with φ

2.4 Theoretical thermal conductivity of nanofluids

Several semi-empirical correlations have been proposed to determine theoretical conductivity two-phase mixtures. Classic theory of two component system is applied.

Maxwell on the basis of 'effective medium theory'analysed the heat conduction for solid-in-liquid suspensions as follows [2,8].

$$K_e = \left[\frac{2k_l + k_p + 2\emptyset(k_p - k_l)}{2k_l + k_p - \emptyset(k_p - k_l)}\right] k_l \qquad (1)$$

Where k_e; k_p; k_l represent the effective, particle and liquid thermal conductivity and Φ, is the particle volume fraction.

Another relationship used in case of high thermal conductivity ratios is the Hamilton- Crosser model, which involves the use of surface area to volume ratios.

The k_e/k_l is given by

$$\frac{k_p+(n-1)k_b-(n-1)(k_b-k_p)\emptyset}{K_p+(n-1)k_b+(k_b-k_p)\emptyset} \quad (2)$$

2.5 Current scenario of nanofluid related research

Presently, immense research is being carried out in the field of Nano-fluids to use it as a coolant. The major reason behind this being the reduction in size of the cooling systems and efficient thermal conductivity. Yu et al. predicted that around 15-40% enhancement can be brought upon in the heat transfer by using Nano-fluids. This gives a freedom to enhance the design of automobiles [4,9]. This also minimizes the co-efficient of drag and increases the fuel efficiency. Choi also designed a fuel saving project using the Nano-fluid which included smaller and lighter radiators ultimately causing in improved fuel proficiency. The vitalbenefit of using Nano-fluid as coolant is its potential to allow high heat rejection in the automobile industry.

Eastman et al. also calculated the thermal conductivity of nanofluids containing Aluminium and copper nanoparticles with two different base fluids: water and HE- 200 oil. A tremendous sixty percent improvement was visible in the thermal conductivities level. Also, the use of copper nanoparticles (using the one-step method) results in larger improvements than that of CuO (using the two-step method) [3].

Lee et al. suspended Copper and Aluminium oxide nano-particle with two different base fluids: water and ethylene glycol (EG) and obtained four combinations of nano-fluids: CuO in water, CuO in EG, Al_2O_3 in water or in EG. Experimentallyit was found out that having better thermal conductivities than the base fluids without the nano-particles. The CuO/EG mixtureshowed enhancement of more than 20% at 4 volume percentage of nanoparticles. In the low volume fraction range (<0.05 in test), the thermal conductivity ratios increase almost linearly with volume fraction. Although the size of Al_2O_3particle is smaller than that of CuO, CuO nano-fluids exhibited better thermal conductivity values than Al_2O_3-nanofluids [6].

Wang et al. calculated the effective thermal conductivity of nano-fluids by a steady-state parallel-plate technique. The base fluids (water, ethylene glycol (EG), vacuum pump oil and engine oil) contained suspended aluminium and copper oxide nanoparticles. The thermal

conductivity increased with increased concentration of nano-particles and decreasing particle size. The results showed a 12% improvement of the effective thermal conductivity at 3 volume percentage of nanoparticles as compared to 20% improvement reported by *Masuda etal.* and 8% reported by Lee et al. at the same volume fraction of particles [10].

Xuan and Li also researched regarding the thermal conductivity of water using Copper particles of comparatively large size (100 nm) to the same extent as has been found using copper oxide particles of much smaller dimension (36 nm). A suitable selection dispersants may improve the stability of the suspension. They used oleic acid for transformer oil–Copper nano-fluids and salt for water–Copper suspension in their study and found that Cu particles in transformer oil had superior characteristics to the suspension of Copper particles in water [9].

Xie et al. also experimented the effects of the *pH* value of the suspension, the specific surface area (SSA) of the dispersed particles, the crystalline phase of the solid phase, and the thermal conductivity of the base fluid on the thermal conductivity of nanofluids. They found that the increase in the difference between the *pH* value and isoelectric point (the pH at which a molecule carries no net electrical charge) of Al_2O_3 resulted in the enhancement of the thermal conductivity. The specific surface area (SSA) of the nanoparticles plays an influential role in the thermal conductivity of the Nano-fluids. However, the crystalline phase of the nanoparticles did not seem to have any effect on the thermal conductivity of the suspensions [11].

To add to that, *Eastman et al*. used pure Copper nanoparticles of less than 10 nm size and achieved 40% increase in thermal conductivity for only 0.3% volume fraction of the solid dispersed in ethylene glycol. The increased ratio of surface to volume with decreasing size was found put to be an important parameter. Also, the addition of additive acids may stabilize the suspension and in turn enhance the effective thermal conductivity [12].
An iron Nanofluid was prepared by *Hong and Yang* by using ethylene glycol as base liquid. The nanoparticles with mean size of 10 nm were produced by chemical vapour condensation process. It was found out that the iron nanofluids exhibited higher enhancement of thermal conductivity than Copper nanofluids. It simply meant that the material with high thermal conductivity is not all the time the best contender for the suspension to improve the thermal characteristics of base fluids. Also, it was seen that the change in thermal conductivity with volume fraction is not a liner relationship. He also investigated the effect of the

agglomeration of the iron nanoparticles on the thermal conductivity of nanofluids. They found that the thermal conductivity of nanofluids is directly related to the agglomeration of these nanoparticles which is responsible for the nonlinear relation.

Das et al. also inspected the effect of temperature on thermal conductivity enhancement for nanofluids containing Al_2O_3 (38.4 nm) or CuO (28.6 nm) .The thermal conductivity increased two to four times in the temperature range of 20-50 degree C. The results gave us the idea of the application of nanofluids as cooling fluids for devices with high energy density where the cooling fluid is likely to work at a temperature higher than the room temperature. They also mentioned about the inherently stochastic motion of nanoparticles and the possible explanation for the thermal conductivity enhancement since smaller particles show greater enhancements of thermal conductivity with temperature than do larger particles [3,6,13].

Table 2.2: Current research in the field of Nanofluid synthesis [2]

Summary of experimental studies on thermal conductivity of nanofluids

Investigator	Particles	Size (nm)	Fluids	Observations
Eastman et al.	Al_2O_3/CuO/Cu	33/36/18	water, HE-200 oil	60% improvement for 5 vol% CuO particles in water
Lee et al.	Al_2O_3/CuO	24.4,38.4/18.6,23.6	water, EG	20% improvement for 4 vol% Cuo/EG mixture
Wang et al.	Al_2O_3/CuO	28/23	water, EG, PO, EO	12% improvement for 3 vol% Al_2O_3/water nanofluids
Das et al.	Al_2O_3/CuO	38.4/28.6	water	2–4 fold increase over range of 21 °C to 52 °C
Xie et al.	Al_2O_3	12.2–302	water, EG, PO	pH value, SSA, crystalline phase
Li and Peterson	Al_2O_3/CuO	36/29	water	enhancement with volume fraction and temperature
Xuan and Li	Cu	100	water, oil	successful suspension of relatively big metallic nanoparticles
Eastman et al.	Cu	<10	EG	40% increase for 0.3 vol% Cu-based nanofluids
Hong and Yang	Fe	10	EG	18% increase for 0.55 vol% Fe/EG nanofluids
Patel et al.	Au, Ag	4, 15/70	water, toluene	size, temperature, and chemical characteristics
Murshed et al.	TiO_2	∅10 × 40, ∅15	DW	33% and 30% increase at 5 vol% for ∅10 × 40 and ∅15, respectively
Xie et al.	SiC	∅26, 600	water, EG	15.8% increase at 4.2 vol% for ∅26 SiC–H_2O and 22.9% at 4 vol% for ∅600 SiC–H_2O
Choi et al.	MWNTs	∅25 × 50 μm	oil	exceed 250% at 1.0 vol%
Biercuk et al.	SWNTs	∅3–30	epoxy	125% at 1.0 wt%
Xie et al.	TCNTs	∅15 × 30 μm	DW, EG, DE	19.6%, 12.7%, and 7.0% increase at 1.0 vol% for TCNT/DE, EG, and DW, respectively
Choi et al.	SWNTs	∅20–30 × 200	epoxy	300% at 3 wt% SWNT loading
Wen and Ding	CNTs	∅20–60 × ~ 10 μm	water	23.7% ans 31% increase at 0.84% CNT concentration for 20 °C and 45 °C, respectively
Assael et al.	MWNTs, DWNTs	∅130 × 10 μm	water	34% increase for 0.6 vol% suspension
Liu et al.	CNTs	∅20–30	EG, EO	12.4% for EG at 1 vol%, 30% for EO at 2 vol%

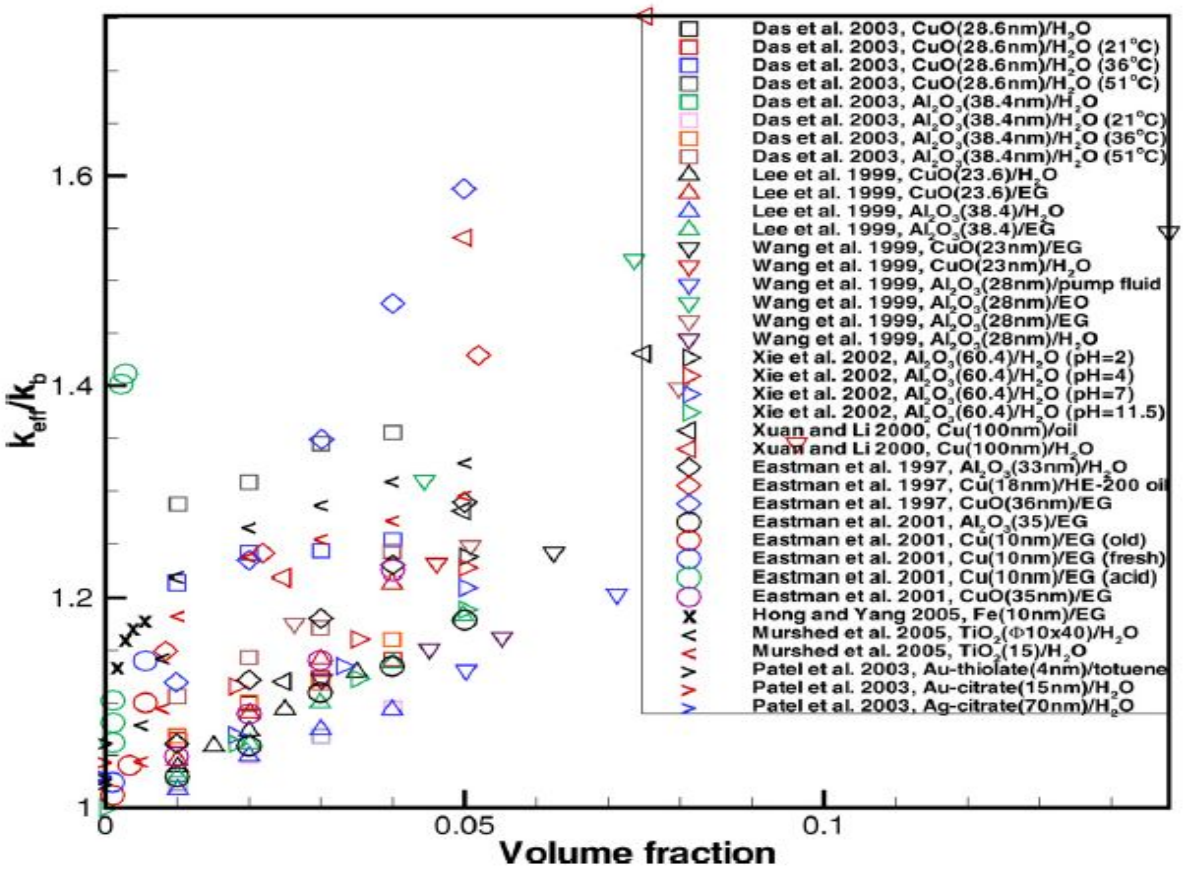

Fig. 2.2: improvement of K_e in various Nanofluid research [2]

2.6 Objectives

The objective of the present study is to develop water and ethelyne glycol base silica dispersed nanofluid in its thermal characteristic study with absence and presence of surfactant. The detailed objectives are listed below:

- Development of nanometric silica powder and characterization of the powder.
- Preparation water and ethyl glycol based nanofluid
- Study the effect of silica concentration and surfactant (oleic acid) on the thermal conductivity of the prepared fluids
- Stability study of the prepared fluids
- Correlation of the parameters with the stability and conductivity

CHAPTER III: Experimental

3.1 Materials

Silica sand of around 2000 grams was collected from construction site. The sand was washed to remove soluble salts, impurities and low density organic materials. The sand sample was dried in the air.Progressive meshing was done using meshes of sieve size 50 and 72 to obtain particles of -72 mesh size. This gave silica particles having size less than 200 microns. About 200 grams of -72 mesh silica was collected to undergo size reduction in ball mill and nanofluid synthesis.

The silica powders ere further processed for nanofluid preparation and subsequent characterization as per the flow chart shown in Fig. 3.1

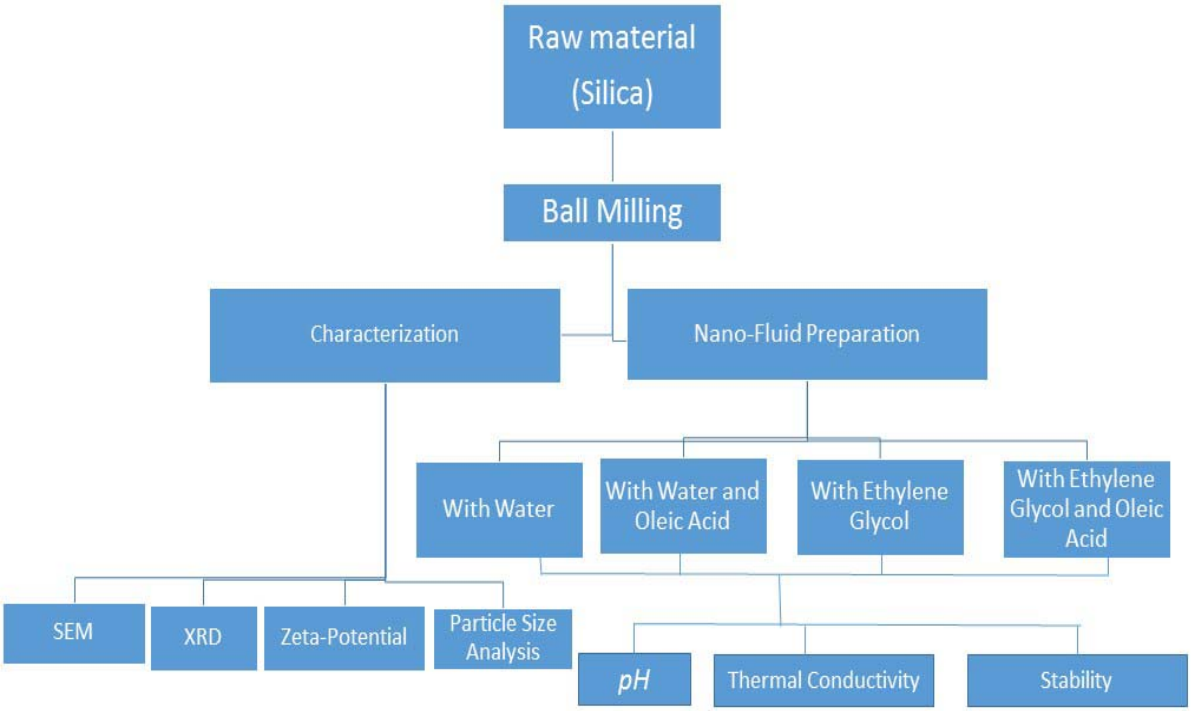

Fig. 3.1: Flow chart of experimental procedure

3.2 Powder Synthesis (Ball milling)

Further size reduction in the sample was done using a high energy tumbler ball mill. The milling containers were thoroughly cleaned to prevent contamination of the sample. The reduction was done using steel balls which were also cleaned and dried using acetylene .each of the bowl was filled with steel balls and silica sample with ball to powder ratio of 10:1. Hence each container contained 1 kg of steel balls and 100gm of silica powder. The containers were sealed and properly locked in the milling machine. Dry milling of the silica sample was done for 30 minutes and intermediate cooling cycles of 45 minutes. Milling was done for a total time of 4 hours. The nano powder obtained was stored in an air tight container to prevent contamination and agglomeration. Thus, the important parameters while ball milling were milling atmosphere, ball to powder ratio, time of milling, milling temperature, milling media etc.

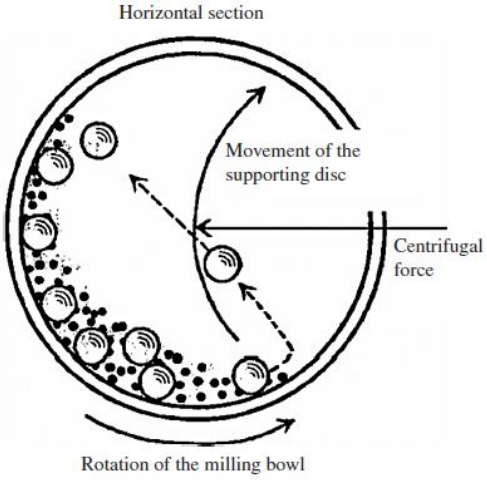

Fig. 3.2: Schematic of ball milling procedure

3.3 X-ray Diffraction Analysis

The before and after milled powder was analysed by X-ray Diffraction study using PHILIPS diffractometer. The range of scanning (2 theta value) was from 20 to 100 degrees. Continuous scanning was done with generator settings of 35kV and 30 mA. The data thus obtained was analysed using Xpert analyser and the respective *d* spacing and FWHM (Full Width Half

Maximum) were calculated for the desired peaks. Then, the crystallite size was calculated using Scherer equation as given below:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \qquad (3)$$

Where:

τ=mean size of the crystalline grains

K= dimensionless shape factor, with a value close to unity.

λ=X-ray wavelength;

β=line broadening at half the maximum intensity (FWHM),

θ=Bragg angle.

3.4 Zeta potential

Zeta potential was used to measure the magnitude of electrostatic charge repulsion/attraction between particles. The silica sample was taken in small amount and mixed with distilled water. The mixture was sonicated using a sonicator to disperse the silica particles uniformly in water. The zeta potential of the dispersion was measured at different *pH*. The *pH* of the dispersion was varied adding drops of nitric acid of standard concentration. The *pH* was measured using a *pH* meter. The sample was again sonicated to prevent any settling of the silica particles. Then the zeta potential of the sample at that *pH* was measured using a zetasizer.The zeta potential was measured at 5 different *pH* values and the variation was achieved adding weak acid or base to the dispersion. The *pH* variation with potential was plotted to extract the iso-electric point (IEP).

3.5 Particle size analysis by zetasizer

The particle size distribution and the average particle size of silica was measured using the zetasizer at the natural *pH*value of silica. The plots obtained were of intensity vs size and

volume vs size. To measure the average particle size in the dispersion the parameters used were refractive index = 1.54 and absorption coefficient = 0.01.

3.6 Scanning Electron Microscopy

The milled and unmilled sample was examined using ICON make Field Emission Scanning electron microscope (FESEM). The four crucibles were initially cleaned using acetone and dried. Carbon tape was mounted on the crucibles .The unmilled and milled samples of silica were sprinkled on the carbon tape. The excess of powdered sample was blown off and then the samples were loaded in the SEM. The chamber was evacuated and then the powder samples were observed at different magnification and contrast settings. For unmilled samples images were taken at magnifications of 200X, 400 X and 800X were used. For milled samples images were taken at high magnifications of 15000X, 50000X and 100000X. The reduction in particle size was evaluated using software.

3.7 Nanofluid preparation

Silica dispersions were made with 0.05 %, 0.1 %, 0.2%, 0.5% and 0.8% volume percent in Ethyl Glycol and distilled water and base solvents. 30ml test tubes were taken and filled up to 28 ml and then calculated amount of silica was added to each test tube. The samples were sonicated using a sonicator for about an hour. Control samples of pure distilled water and pure Ethyl Glycol was also made. To check the effect of surfactant, oleic acid (0.16vol %) was also added to one set of such fluids. Table 3.1 shows the summery of

Table 3.1: Summary of prepared Nanofluid

Base solvent	Silica Volume Percentage	Surfactant (oleic acid)
Distilled Water	0.05%, 0.1 % ,0.2% ,0.5%,0.8%	0,0.16 vol. %
Ethyl Glycol	0.05%, 0.1 % ,0.2% ,0.5%,0.8%	0,0.16 vol. %

3.8 Thermal conductivity study

The test tube samples were fitted with corks and thermal conductivity probe (KD 2 Pro) was inserted through the cork. The thermal conductivity of the sample was measured across the length of the probe. The thermal conductivity of the sample were noted at room temperature. After measuring thermal conductivity of the sample the corresponding *pH* of the sample was also recorded using a portable *pH* measuring instrument. The *pH* and thermal conductivity probes were cleaned with acetone after each measurement to avoid contamination. After this 0.5 ml of Oleic acid was added to each solution and sonicated for 1 hour. Again the pH and thermal conductivity was measured for each sample. The change in conductivity of samples was observed. The experimental setup is as shown in Fig.

Fig. 3.3: Thermal conductivity instrument KD 2 Pro with different probes

3.9 Stability study

The stability of the prepared silica dispersed nanofluid of in water and ethyl glycol was studied over 24 hours of time. The fluid was kept in rest and after each pre determined time gap visual observations was made for 24 hours to check the stability, i.e. to check the settling of the silica particles. After the addition of oleic acid the stability of the dispersions were again observed. The time taken by the silica particle to settle down was reported qualitatively (in hours).

CHAPTER IV: RESULTS AND DISCUSSION

4.1 Particle Size Analysis

4.1.1 By Scanning Electron Microscope

4.1.1.1 Before Milling

The SEM images were taken at various degrees of magnification and particle size was calculated at 200x magnification. The particle size was found out to be in the range of 180-240 micro-meter.

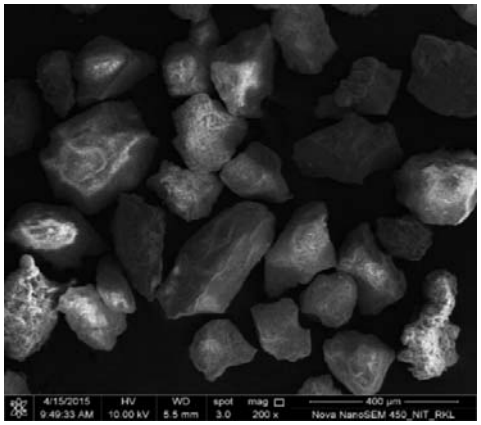

Fig.4.1

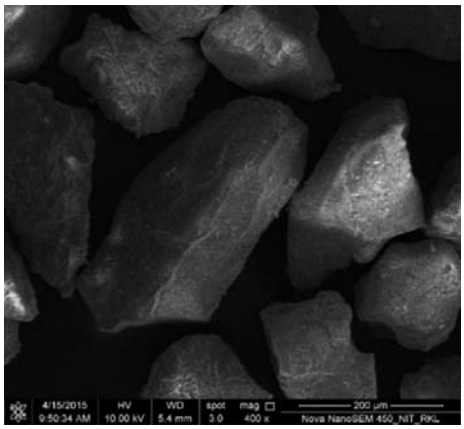

Fig.4.2

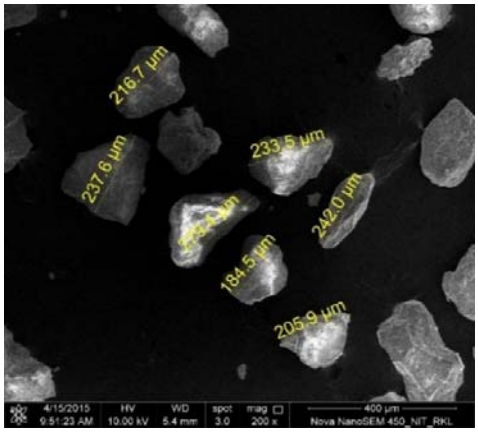

Fig 4.3

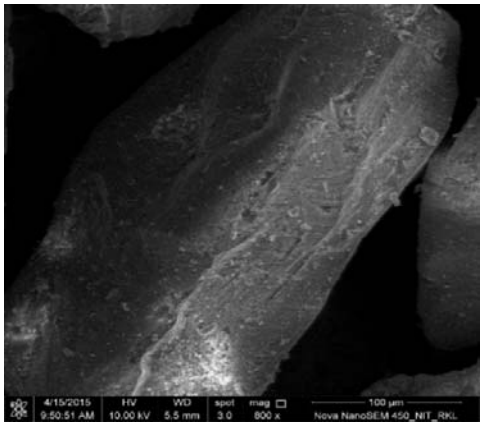

Fig 4.4

Fig. 4.1: SEM image at 200x magnification. Fig. 4.2: SEM image at 400x magnification.Fig. 4.3: SEM image at 800x magnification. Fig. 4.4: Particle Size Analysis at 200x magnification.

4.1.1.2 After Milling

The SEM images of the milled powders were taken at various degrees of magnification and particle size was calculated at 15000x magnification. The particle size was found out to be in the range of 250-400 nm.

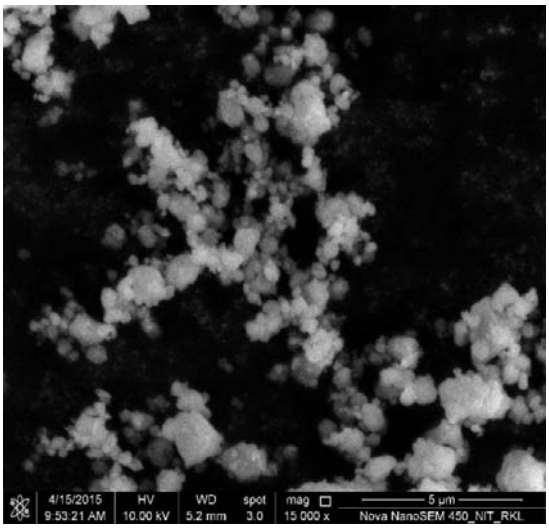

Fig.4.5

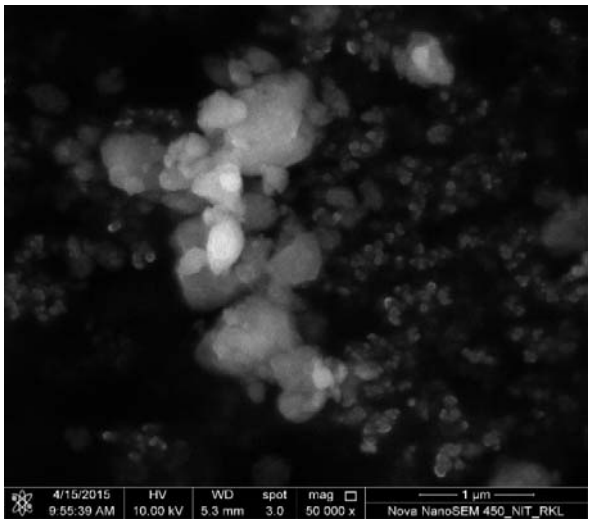

Fig.4.6

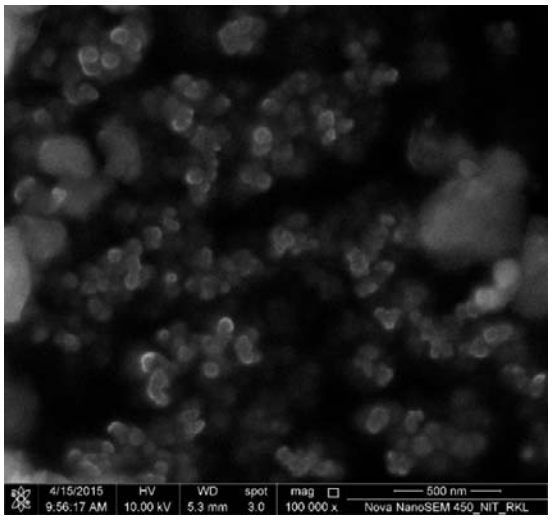

Fig.4.7

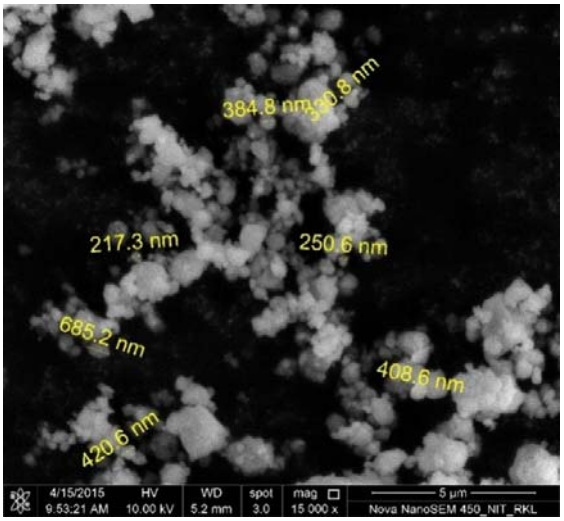

Fig.4.8

Fig. 4.5: SEM image at 15000x magnification. Fig. 4.6: SEM image at 50000x magnification. Fig.4.7: SEM image at 100000x magnification. Fig. 4.8: Particle Size Analysis at 15000x magnification.

Thus, from the figures it is clear that after milling there has been a reduction in size in the ratio of 600-700. This ratio depends upon various factors such as the type of ball mill used, milling media, ball material and weight ratio of the ball and powder. The final particle size in the above experiment is in the range of nano-meters which is appropriate for the nano-fluid preparation. The particle size plays an important role in determining its cooling properties and stability at various concentration as particle plays a vital role to keep in suspension. Moreover, from the figure it was also observed that particles were uniform in size (nano distribution of size) and shape. These are also highly essential for good stabilization of the particles in a fluid.

The SEM images give us an idea about the brittle mode of fracture of the ceramic material. As a result of which the required milling time is very low in this case as compared to other milling processes. It is clearly evident in Fig.4.7 and Fig.4.8 that if we reduce the particle size any further, then there will be agglomeration which is highly detrimental and thus further milling was avoided.

4.1.2 By Zeta-sizer after milling

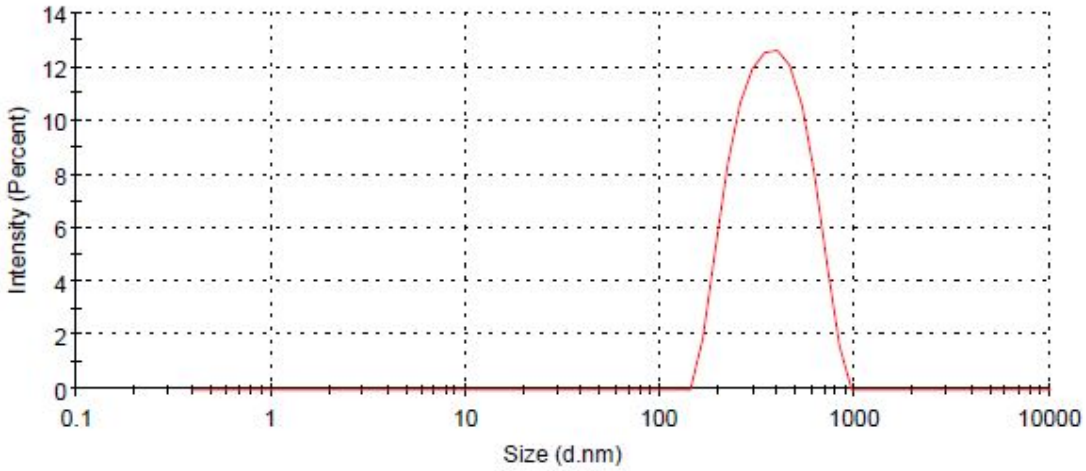

Fig. 4.9: Particle Size (d, diameter) distribution by Intensity

Fig. 4.9 shows the particle size distribution of the milled silica powder as obtained from zetasizer instrument based on intensity function. From the above graph, only one peak at 394nm size was observed which indicates presence of sharp normal distribution of powder size after milling. The average particle size calculated from the weighted average was around

487 nm.It is preferred to determine the particle size using a Zetasizer because its accurate, reliable and repeatable particle size analysis in one or two minutes and the measurement can be done in the native environment. It uses the technique of dynamic light scattering and the determination of the mean size only requires knowledge of the viscosity of the liquid. Also it required not much sample preparation.Minor difference between this observation and SEM study may be due to slight agglomeration during the characterization.

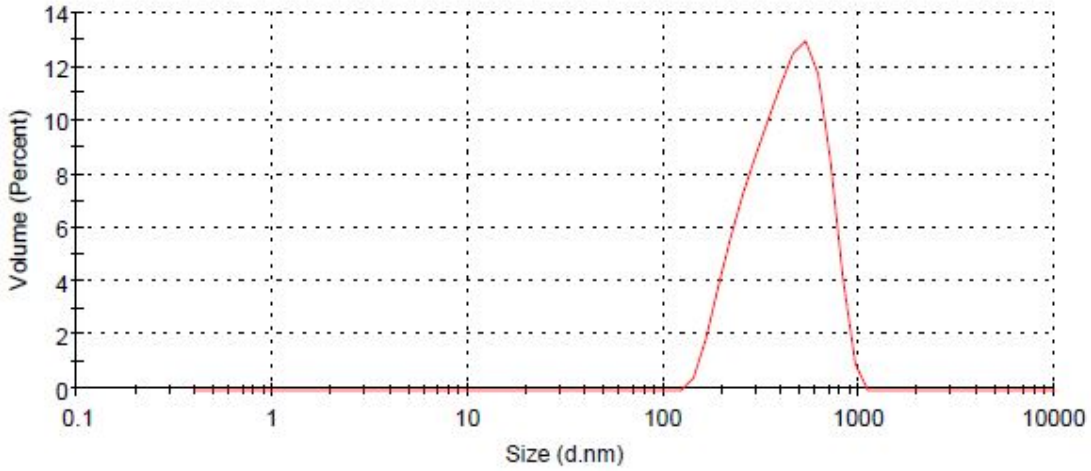

Fig. 4.10: Particle Size (d, diameter) distribution by Volume Percentage

Fig. 4.10 displays similar result as of Fig. 4.9 but with calculation made based upon volume percentage. From the above graph also, one single peak at 449nm size was observed and the average comes out to be around 487 nm.So Zetasizer being the more accurate measurement technique among the two processes used, we will consider the mean size of the particles to be around 487 nm throughout the experiment,

4.2 X-Ray Diffraction

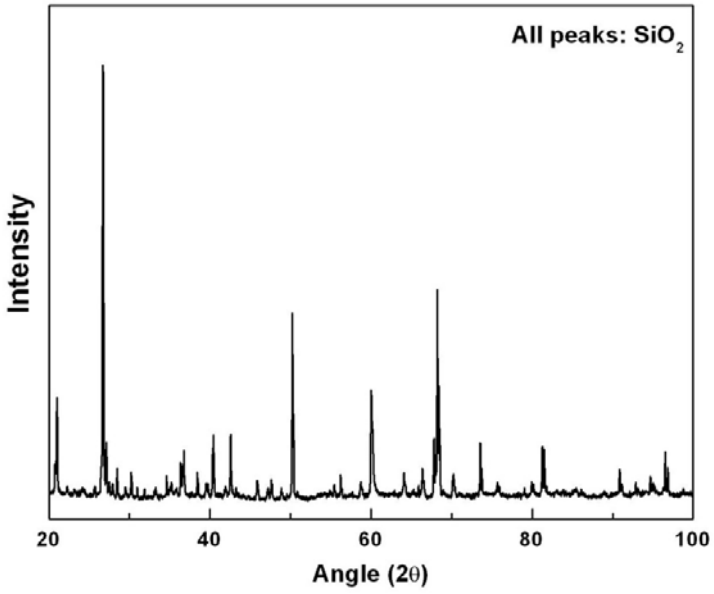

Fig. 4.11: XRD of unmilled sample of SiO_2

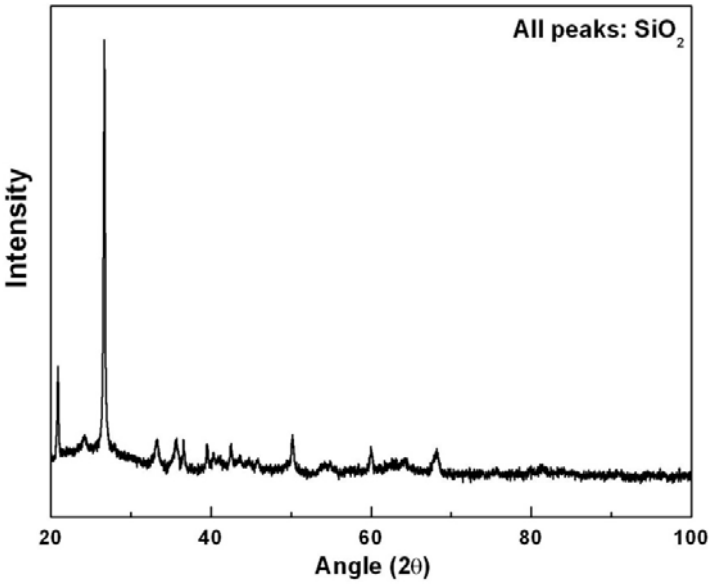

Fig. 4.12: XRD of milled sample of SiO_2

Figure 4.11 and 4.12 display the XRD plot of unmilled and milled powder. Both the plots show only crystalline Silica peaks. But in Fig. 4.12 the number of visible peaks has been decreased. During milling, incorporation of lattice strain and grain size reduction is common phenomena. These in turn increases the peak width, which in turn reduces the intensity of the peaks at a particular scale of intensity. Thus, figure 4.12 displays peak broadening due to milling operation. To enumerate the broadening effect, from FWHM of the highest intensity peak the grain size of milled silica was calculated by Debye Scherermethod. And is was found to be252 nm.

4.3 Zeta Potential measurements

Table 4.1: pH vs. zeta potential

pH	Zeta potential (in mV)
2	2.9
3.4	4.11
5	3.1
6.9	-33

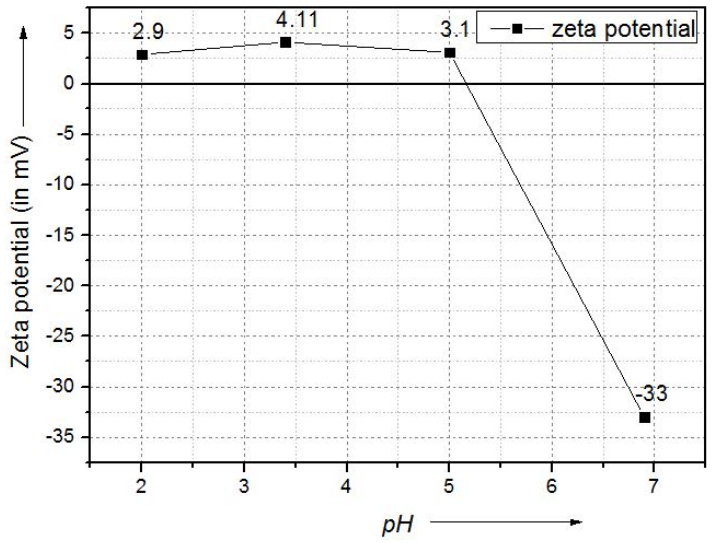

Fig. 4.13: Iso -electric point estimation from extrapolation of zeta potential

The zetasizer was used to measure the iso-electric point (IEP) of the silica solution. The *pH* vs zeta potential plot as shown in Fig. 4.13 displays 5.1*pH* at zeta potential value zero.Thus, the obtainediso-electric point of the milled silica was about 5.7*pH*. The synthesis of nano-fluid should be either done above this *pH* or below this *pH* to increase the surface charge which in turns increases the stability of the suspension by repulsion between each other reducing the chance of agglomeration. This is because at the iso-electric point the net charge on the surface of the nanoparticle is 0 and hence they will not disperse and hence coagulate.

4.4 Thermal Conductivity

Table 4.2: Variation of conductivity of silica in water and Ethyl Glycol and addition of oleic acid

	Sample	Observed Conductivity(W/mK)	Theoretical Conductivity(W/mK)	Oleic acid added(0.5ml)
1	Pure Water	0.69	0.69	no
2	0.05%+water	1.128	0.693	no
3	0.10%+water	1.042	0.696	no
4	0.20%+water	1.25	0.702	no
5	0.50%+water	1.417	0.720	no
6	0.80%+water	1.014	0.740	no
7	Pure Ethylene	0.423	0.423	no
8	0.05%+EG	0.554	0.424	no
9	0.10%+EG	0.76	0.426	no
10	0.20%+EG	0.704	0.429	no
11	0.50%+EG	0.484	0.443	no
12	0.80%+EG	0.407	0.447	no
13	0.05%+water	1.15	0.69	Yes
14	0.10%+water	1.193	0.693	Yes
15	0.20%+water	1.175	0.696	Yes
16	0.50%+water	1.401	0.702	Yes
17	0.80%+water	1.121	0.720	Yes
18	0.05%+EG	0.559	0.424	Yes
19	0.10%+EG	0.495	0.426	Yes
20	0.20%+EG	0.737	0.429	Yes
21	0.50%+EG	0.45	0.443	Yes
22	0.80%+EG	0.424	0.447	Yes

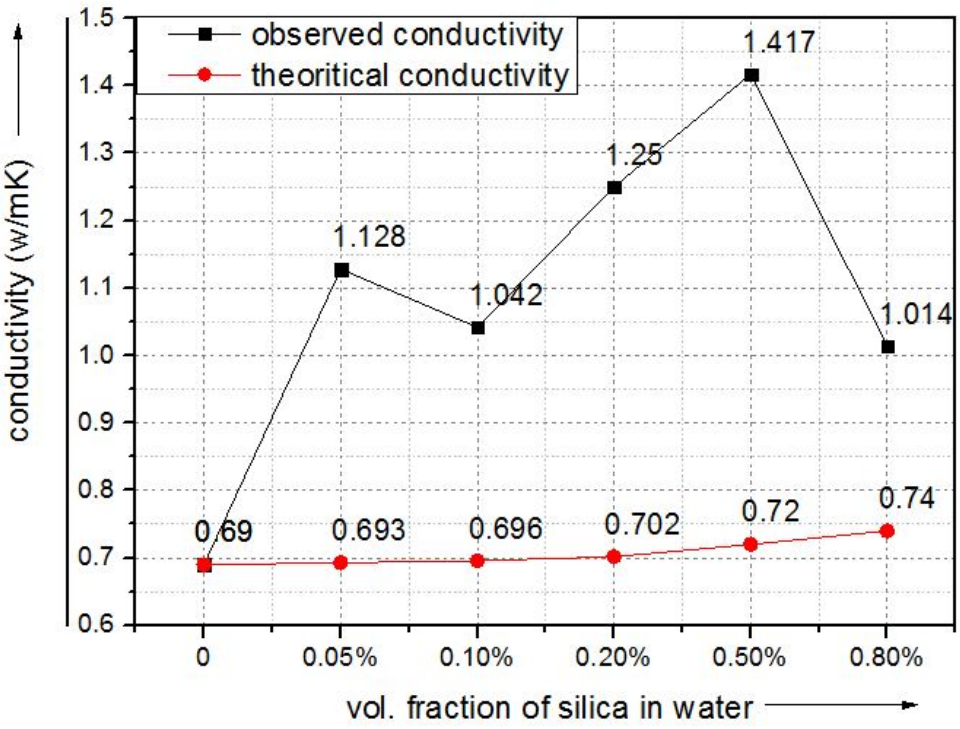

Fig. 4.14: Theoretical and observed conductivity of silica –water solution

Fig.4.14 gives us an idea about the trend in the variation of thermal conductivity with change in volume fraction of Silica in water. The theoretical value of the thermal conductivity calculated from Maxwell Theory is plotted against the experimental values. It is evident that the thermal conductivity gradually increases with increase in Silica's volume fraction in case of theoretical values and the same trend is observed in the experimental data. The slight decrease after 0.05% volume fraction can be due to certain unavoidable glitches during experimental procedure. After, 0.5% of Silica's volume fraction, there is sudden decrease in the thermal conductivity. This is due to the agglomeration of the nano-particles into larger lumps such that they become heavy and settle down and thus the stability of the solution decreases. Incorporation of large amount of ceramic particle actually congesting the liquid, i.e. the mean distance is forcibly decreased. This counters the repulsive force offered by surface charge. Add thus, increasing amount of SiO_2 ultimately shows a reduction in conductivity.

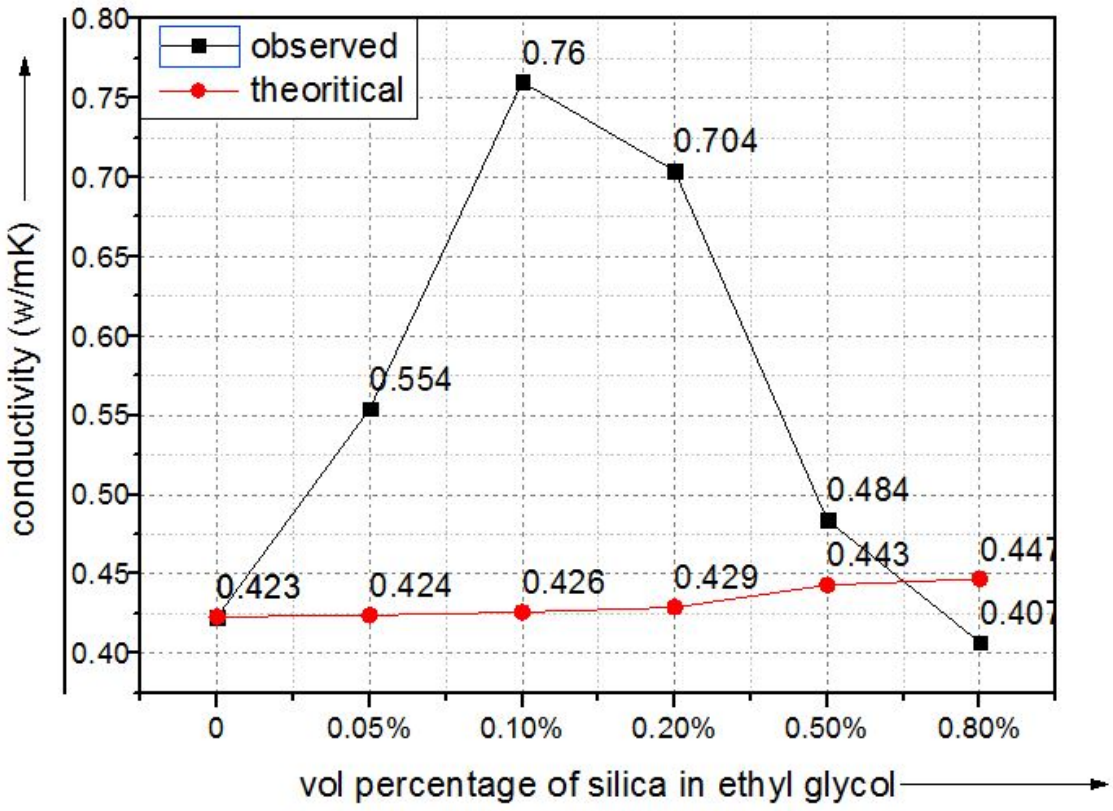

Fig. 4.15: Theoretical and observed conductivity of silica –EG solution

Fig.4.15 gives us an idea regarding the variation of thermal conductivity of Ethylene Glycol with volume percentage of Silica nano-particles in it. The trend of the theoretical values are same as that in fig.4.14; however the agglomeration of the nano-particles, resulting in larger lumps, decreased stability and thermal conductivity, takes place at a lower value of Silica's volume fraction. Thus, the allowable or preferable volume fraction of silica in ethylene glycol solution to make an efficient coolant is relatively low as compared to that with water as the base fluid.

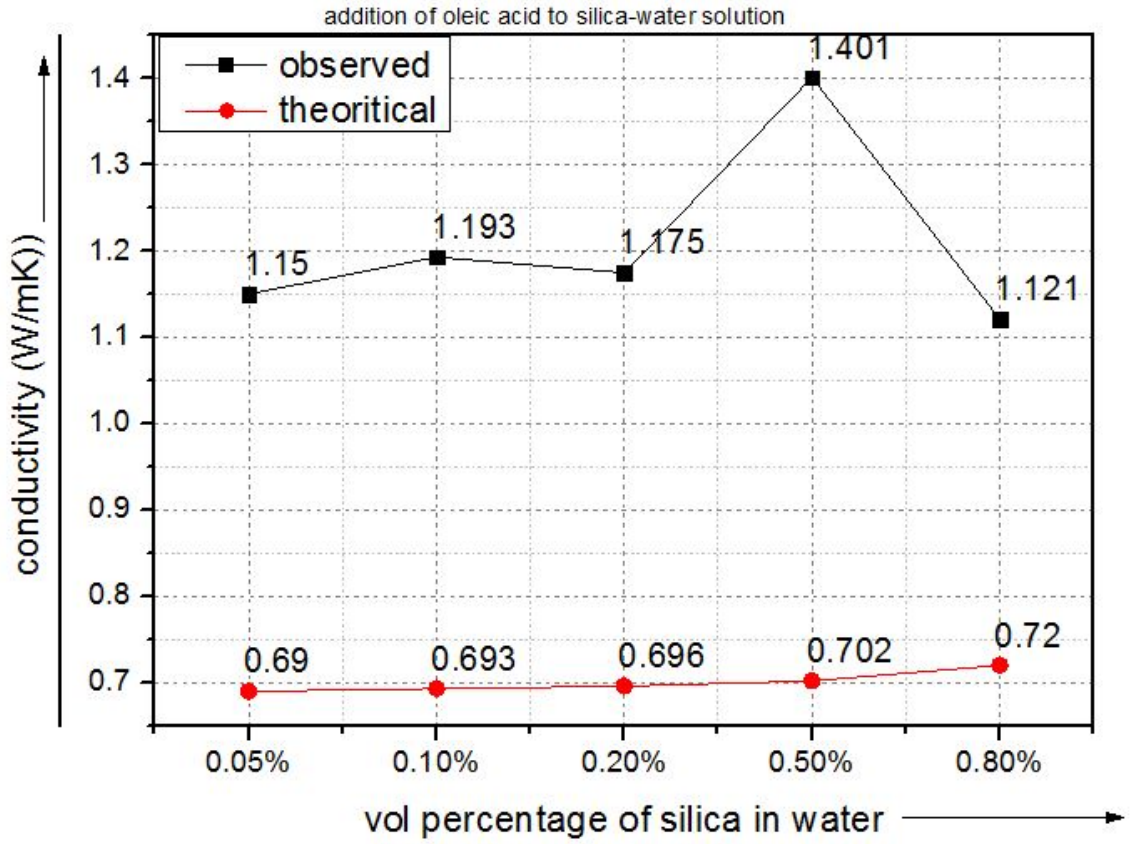

Fig. 4.16: Theoretical and observed conductivity of silica –water solution on addition of 0.5ml oleic acid

Fig.4.16 shows the variation of thermal conductivity of water solution having silica nano-particles with the addition on Oleic acid across various volume percentage of Silica addition. Comparing Fig. 4.14 and 4.16 it was observed that there is no prominent effect in of oleic acid on thermal conductivity value; but, the change is conductivity with SiO_2 content is less effective in presence of oleic acid. So, this acts as stabilizing agent, i.e. prevents agglomeration of the suspended particles. To sum it up, the addition of Oleic acid increases the efficiency of using the nano-fluid as a coolant and also the required Silica amount for maximum conductivity decreases.

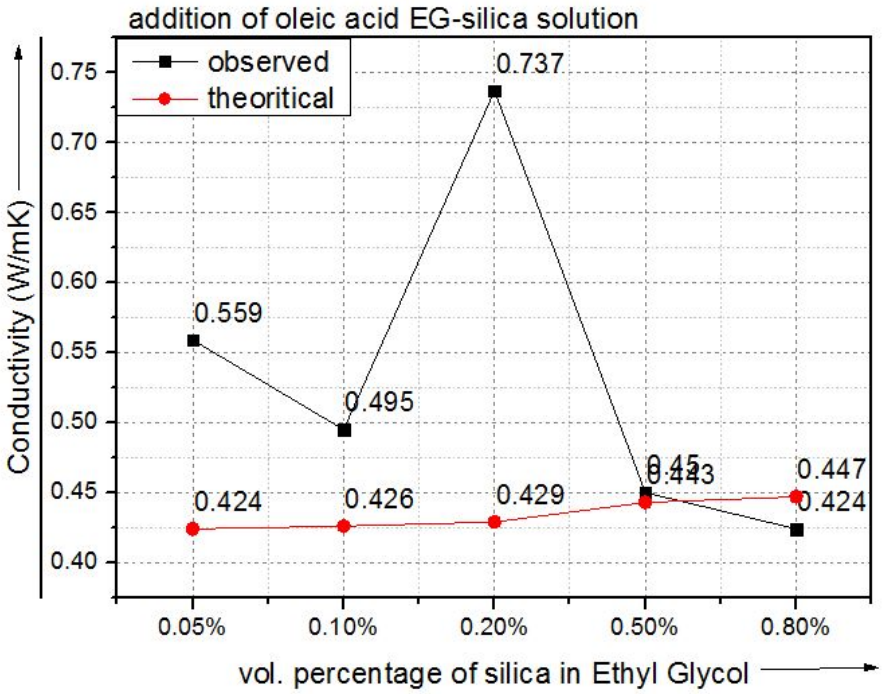

Fig. 4.17: Theoretical and observed conductivity of silica –EG solution on addition of 0.5ml oleic acid

Fig.4.17 represents the variation of thermal conductivity of Ethylene Glycol with addition of Silica nano-particle along with Oleic acid across various volume fraction of Silica. The trend is same as that of fig.4.16. The major difference comes in the value of maximum thermal conductivity (relatively lower in case of EG as base fluid) and preferable Silica's volume fraction to prevent agglomeration (decreases with addition of Oleic Acid).

In all the plots (from fig.4.14 to fig.4.17), there is a difference in the thermal conductivities of the solution in theoretical and experimental data. This is because, while calculating the theoretical values, we do not take into account the interaction of the added nano-particle or surfactant with the base fluid. The Maxwell theory, used for calculating the theoretical values considers only two-phase system and doesn't consider other various interactions taking place inside the system. These interactions affect the thermal conductivity values as well and thus there is a difference in the theoretical and experimental data. To add to that, in our sample preparation, there is a possibility of impurity additions during the forming processes which also affects the thermal conductivity by undergoing various reactions or interaction with the base fluid, silica nano-particles or surfactant used.

4.5 pH measurements

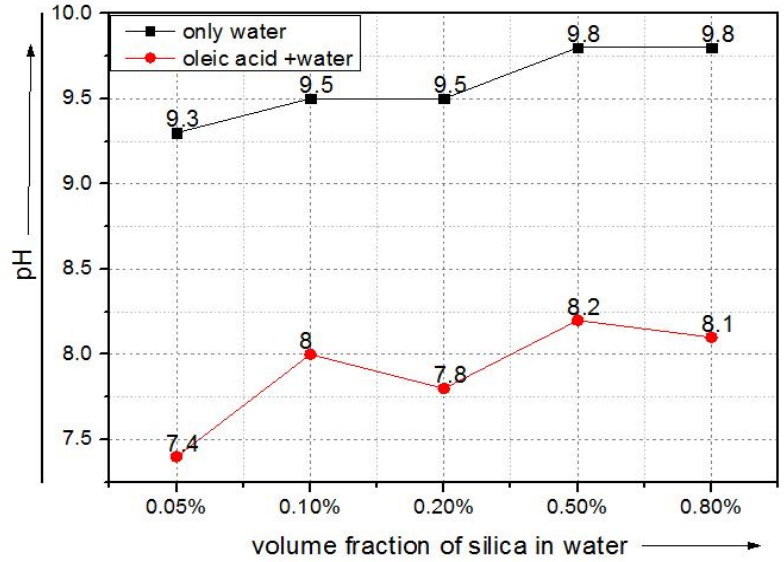

Fig. 4.18: *pH* variation of silica water solution and on addition of oleic acid

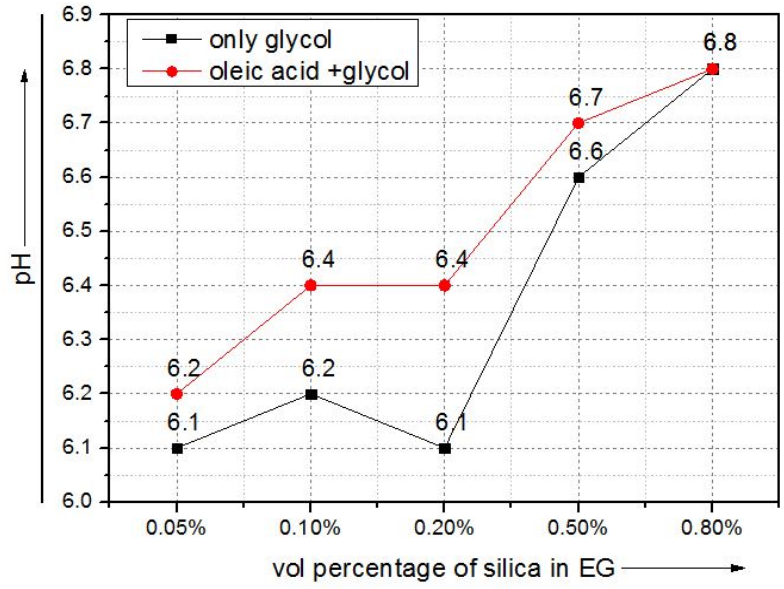

Fig. 4.19: *pH* variation of silica EG solution and on addition of oleic acid

Fig.4.18 and Fig.4.19 show the trend in the variation of *pH* with volume fraction of Silica in the base fluid (Water and EG respectively). It is observed that there is slight change in the *pH*value with addition of Oleic acid. In case of water as the base fluid, with addition of Oleic acid the *pH* value decreases as the solution becomes more acidic and it modifies the surface charge. But in case of EG as the base fluid, the *pH* value remains almost same after addition of oleic acid. As the change of *pH* with addition of oleic acid has no direct effect on conductivity, it can be concluded that oleic acid has surfactant effect apart from modification of *pH*.

4.6 Stability study

Table 4.3: Stability of silica –water/EG solutions with /without addition of oleic acid

Sample (silica –H_2Osolution)	**Stability (2 Hours)**	**Stability (4 Hours)**	**Stability (24 Hours)**
0.05%+water	Unstable	Unstable	Unstable
0.10%+water	Unstable	Unstable	Unstable
0.20%+water	Unstable	Unstable	Unstable
0.50%+water	Unstable	Unstable	Unstable
0.80%+water	Unstable	Unstable	Unstable
Sample (Silica –EG Solution)	Stability (2 Hours)	Stability (4 Hours)	Stability (24 Hours)
0.05%+EG	Unstable	Unstable	Unstable
0.10%+EG	Unstable	Unstable	Unstable
0.20%+EG	Unstable	Unstable	Unstable
0.50%+EG	Unstable	Unstable	Unstable
0.80%+EG	Unstable	Unstable	Unstable
Sample (addition of oleic acid)	Stability (2 Hours)	Stability (4 Hours)	Stability (24 Hours)
0.05%+water	Stable	Stable	Unstable
0.10%+water	Stable	Stable	Unstable
0.20%+water	Unstable	Unstable	Unstable
0.50%+water	Unstable	Unstable	Unstable
0.80%+water	Unstable	Unstable	Unstable
Sample (addition of oleic acid)	Stability (2 Hours)	Stability (4 Hours)	Stability (24 Hours)
0.05%+EG	Stable	Stable	Stable
0.10%+EG	Stable	Stable	Stable
0.20%+EG	Unstable	Unstable	Unstable
0.50%+EG	Unstable	Unstable	Unstable
0.80%+EG	Unstable	Unstable	Unstable

The above table is made in accordance to visual observations. On comparing these values with that of fig.4.14 – fig.4.19; it can be concluded that the relative stability of the solution is closely related with that of the visual observations. The addition of Oleic acid helps in increasing the stability of the solution. With increase in the volume fraction of Silica addition, the amount of oleic acid needed to stabilise the solution also increases. Addition of oleic acid also interacts with the surface and varies the surface charge which in turn enhances the thermal conductivity of the solutions.

CHAPTER V: CONCLUSIONS

- For as –received silica powder with starting range of 180-250 μm was successfully ball milled to reduced size of 240-400nm.

- Due to milling there was also reduction of grain size to a value of 252nm.Iso-Electric Point (IEP) of the powder was found to be at 5.1 *pH.*

- Nanofluid with H_20 and Ethylene Glycol base were prepared by dispersing the milled powder in presence and absence of Oleic Acid.

- Increasing the amount of silica in Nanofluid increase the thermal conductivity both for H_2O and EG as base fluid up to a certain value of SiO_2 content .This specific value is lower for EG.

- Oleic Acid addition doesn't change the thermal conductivity values to a great extent but it decreases the effect of SiO_2 content on thermal conductivity.

- Charge in SiO_2 content and addition of oleic acid affect the *pH* value of fluid which in turn affect the stability of the fluid.

- Visual stability test showed stable dispersion (after 24 hours for EG and 4 hours for H_2O when oleic acid was added).

CHAPTER VI: REFERENCE

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